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Experimental demonstration of mode-selective phonon excitation of 6H-SiC by a mid-infrared laser with anti-Stokes Raman scattering spectroscopy

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Mode-selective phonon excitation by a mid-infrared laser (MIR-FEL) is demonstrated via anti-Stokes Raman scattering measurements of 6H-silicon carbide (SiC). Irradiation of SiC with MIR-FEL and a Nd-YAG laser at 14 K produced a peak where the Raman shift corresponds to a photon energy of 119 meV (10.4 μm). This phenomenon is induced by mode-selective phonon excitation through the irradiation of MIR-FEL, whose photon energy corresponds to the photon-absorption of a particular phonon mode. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4827253]

Wide-gap semiconductors, such as SiC, ZnO, and TiO_2, are attractive materials for high power devices, transparent conductive thin films, photocatalysts, etc. They have been well studied to improve their physical properties (e.g., electron mobility and electronic resistance). Because the interaction between the phonon mode and carrier such as an electron (electron–phonon interaction) plays an important role in the physical properties of wide-gap semiconductors, the electron–phonon interaction must be clarified to realize high-performance devices.[1–4] Consequently, a method to control the phonon mode (mode-selective phonon excitation) would be a powerful tool.[5,6]

One method for the mode-selective phonon excitation is through a coherent phonon, which is generated by a pulse laser with pulse width shorter than the vibration period.[7,8] Mode-selective phonon excitations using coherent phonons have been reported in strongly correlated electron systems, super-lattices, nanomaterials, semiconductors, etc.[5–12] For example, Yee *et al.* demonstrated mode-selective phonon excitation of the E_1 mode in GaN.[7] Takahashi *et al.* controlled the lattice vibrations of Ba–O and Cu–O chemical bonds of $YBa_2Cu_2O_{7-\delta}$, which is a superconductive material.[8] Hase *et al.* demonstrated mode-selective phonon excitation and relaxation of Bi–Bi, Bi–Sb, and Sb–Sb chemical bonds in BiSb mixed crystal.[11] In these reports, the generated coherent phonon excited a particular phonon mode, mainly in the THz region (far infrared region).

Another method for mode-selective phonon excitation is via a pulse laser with mid-infrared region light. Rini *et al.* used a mid-infrared laser to irradiate $Pr_{0.7}Ca_{0.3}MnO_3$, which is a strongly correlated electron system, to selectively excite the vibration mode of the Mn–O chemical bonds,[13] and they observed a metal–insulator transition phenomenon. Because the metal–insulator transition of $Pr_{0.7}Ca_{0.3}MnO_3$ occurs when the vibration mode of the Mn–O chemical bonds is excited, they demonstrated that the mode-selective phonon excitation is a tool to control the electronic phase by observing a metal–insulator transition. In addition, Forst *et al.* controlled the magnetism of the $La_{0.5}Sr_{1.5}MnO_4$ and demonstrated ionic Raman scattering experimentally by mode-selective phonon excitation with a mid-infrared laser.[14,15] In this way, mode-selective phonon excitation by mid-infrared laser has been used to analyze or control the physical properties.

Because the absorption energies of the phonons in wide-gap semiconductors (e.g., SiC, ZnO, and TiO_2) are located around the mid-infrared region,[16–19] a mid-infrared laser should be well suited for the mode-selective phonon excitation of wide-gap semiconductors. Nevertheless, this hypothesis has yet to be confirmed. Herein, we demonstrate mode-selective phonon excitation of a wide-gap semiconductor via a mid-infrared laser. Because Raman scattering spectroscopy shows the status of a molecular vibration or phonon directly, we employed anti-Stokes Raman scattering spectroscopy to confirm the mode-selective phonon excitation.

Figure 1 shows the principle of the present method for mode-selective phonon excitation. We hypothesized that the material shown in Fig. 1 has three phonon modes. Electrons excited by phonons introduces anti-Stokes scattering, and the intensity of the anti-Stokes scattering light depends on both the population of electrons in the vibration state and the temperature of the material. For a hot material, three peaks are observed in the anti-Stokes Raman scattering spectrum [Fig. 1(a)]. For a cold material, the anti-Stokes Raman scattering at adequately low temperature is not observed because the electron population at the vibration state is too low even at the lowest-energy excited state [Fig. 1(b)]. However, if mid-infrared (MIR) laser irradiation introduces a mode-selective phonon excitation, an electron at a particular vibration state will be excited even at such low temperature [Fig. 1(c)]. In addition to MIR laser irradiation, the anti-Stokes Raman scattering light will be emitted if the probe light is irradiated onto the material because an electron in the vibration state is generated by MIR laser irradiation. For a cold material with MIR laser irradiation, a single peak

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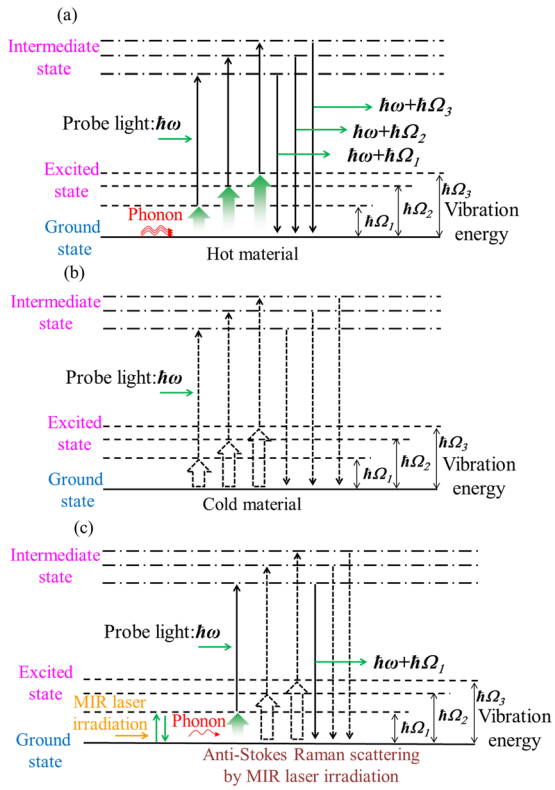

FIG. 1. Schematic of the principle of the anti-Stokes Raman scattering: (a) hot material (b) cold material, and (c) cold material with MIR laser irradiation.

should be observed [Fig. 1(c)]. Therefore, we can demonstrate mode-selective phonon excitation by determining if the peak corresponds to the wavelength of the MIR laser in the anti-Stokes Raman scattering spectrum.

We used a mid-infrared Free Electron Laser (MIR-FEL), KU-FEL (Kyoto University Free Electron Laser),[16] for the phonon excitation. FEL has a specific pulse structure with two types of pulses: macro- and micro-pulses (Fig. 2).

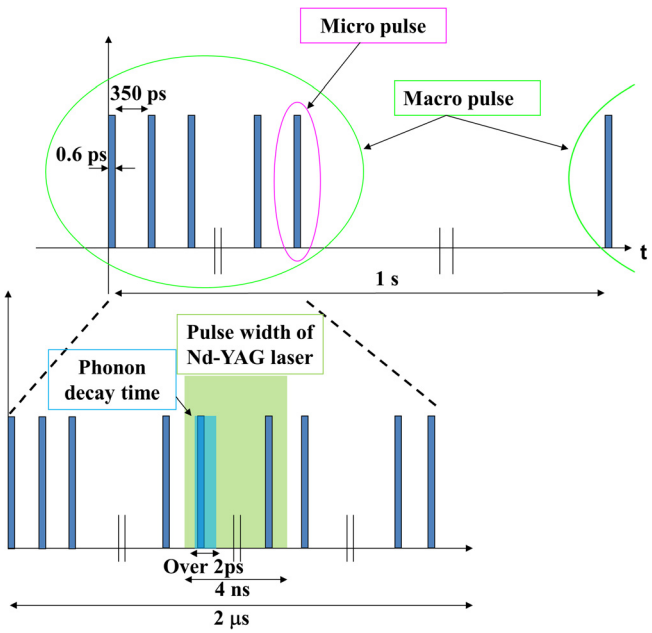

FIG. 2. Relation of the pulse structure between the MIR-FEL and Nd-YAG laser.

A single macro-pulse in KU-FEL contains about 5700 micro-pulses. The pulse duration of the macro-pulse and micro-pulse is 2 μs (FWHM) and 0.6 ps (FWHM) at 12 μm, respectively.[20,21]

In addition, the reported lifetimes of the phonons in wide-gap semiconductors, such as SiC and GaN, are over 2 ps at 293 K, and the lifetime of a phonon at 14 K is about twice as long as that at 298 K.[4,22] To prevent the thermal excitation of the phonons by laser irradiation, the pulse width of the pump laser for phonon excitation must be shorter than the phonon relaxation time for a mode-selective phonon excitation. In this experiment, the pulse width of the micro-pulse of KU-FEL is shorter than the lifetime of the phonon at low-temperature. Therefore, MIR-FEL irradiation induces mode-selective phonon excitation by a photo-excitation effect.

The sample material was commercially available SiC (6H semi-insulator type SiC, Xlamen Powerway Advanced Material Co., LTD: SiC) with dimension of 15 mm $\times$ 15 mm $\times$ 0.33 mm. The SiC (0001) surface was used for the measurement.

Figure 3 shows the experiment setup. A Nd-YAG laser (Gaia-1. Rayture Systems Co., LTD) was used as the probe light. The wavelength, pulse width, and pulse energy were 532 nm (second harmonic generation), 4 ns, and 3 mJ, respectively. The fluence of the Nd-YAG was 130 MWcm^{-2}, and polarization was in the horizontal direction. To cut light from the fundamental wavelength (1064 nm), a short pass filter (SP: high performance OD4 short pass filter, product code: 64333, Edmund optics, cut off: 800 nm) was installed, while a quartz lens focused the laser on the sample surface

A pump laser generated from KU-FEL was focused on the sample by a ZnSe lens ($f = 200$ mm). To cut the inherently generated high harmonics contained in MIR-FEL, a long pass filter (LP: 4.50ILP-25, Andover) was installed before the focusing lens. This experiment employed three irradiation wavelengths, 9.05, 10.4, and 12.5 μm, because 6H-SiC has infrared absorptions at 10.4 μm and 12.5 μm.[16,23] 9.05 μm was selected to investigate the possibility of sum frequency generation (SFG) by MIR-FEL and Nd-YAG laser because 6H-SiC is reported to be a nonlinear optical material.[24,25] The targeted phonon mode was the folded longitudinal optical mode at $x = 0$ (FLO(0)), which is infrared

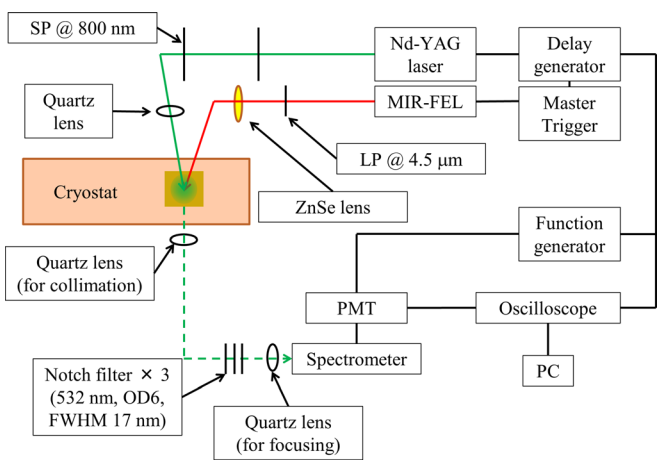

FIG. 3. Schematic of the measurement system for anti-Stokes Raman scattering.

TABLE I. Condition of the irradiated MIR-FEL at each wavelength.

Wavelength of MIR-FEL (μm)	Pulse energy (mJ)	Fluence ($MWcm^{-2}$)
9.05	5	1.67
10.4	5	1.67
12.5	1.5	0.5

active and Raman active, and the wavelength corresponding to the FLO(0) mode is 10.4 μm (970 cm^{-1}). x is the reduced wave vector of the phonon modes in the basic Brillouin zone.[16] The infrared absorption at 12.5 μm corresponds to the folded transverse optical phonon mode at $x = 0$, which is indexed as FTO(0).[16] Table I lists the pulse energy and fluence of the irradiated MIR-FEL at each wavelength.

The emitted light from the sample was collimated by a quartz lens and transferred to a spectrometer. To cut the light from Rayleigh scattering (532 nm), three notch filters (NF53-17 Thorlabs × 2 and StopLine notch filter NF03-532E-25, Opto-line) were used. The Raman scattering light was focused on the entrance slit of the spectrometer by a quartz lens. A photon counting method was used to detect the Raman scattering light by a spectrometer (Triax 190, HORIBA Scientific) and a photomultiplier tube (PMT) with a gating system (R3896 and C1392, Hamamatsu Photonics). The gate of PMT was synchronized with the master trigger of KU-FEL by a function generator. The sample was cooled to 14 K using a closed-cycle Helium refrigerator (cryostat). The measurement data were averaged over 100 trials to obtain one measurement point.

Figure 4 shows the waveforms of the Nd-YAG laser and MIR-FEL. The black line denotes the trigger of the oscilloscope. The pulse width of MIR-FEL (macro-pulse) and

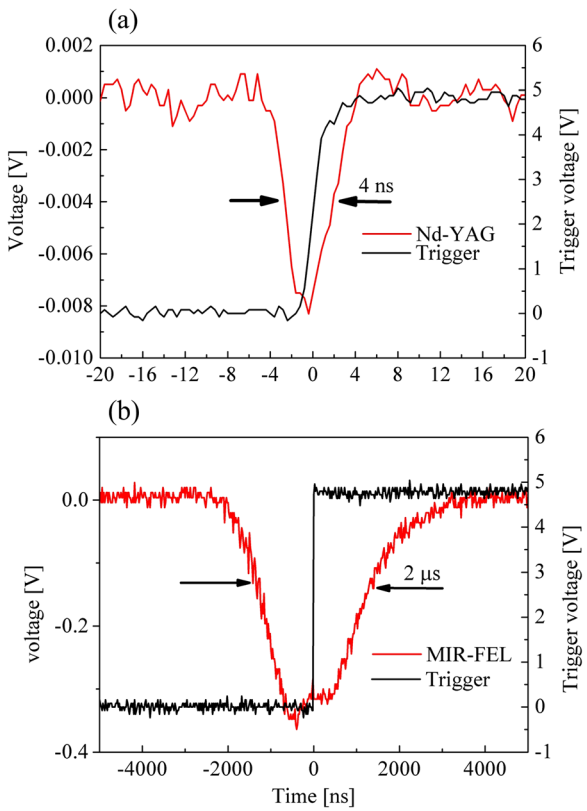

FIG. 4. Waveform and timing of the (a) Nd-YAG laser and (b) MIR-FEL.

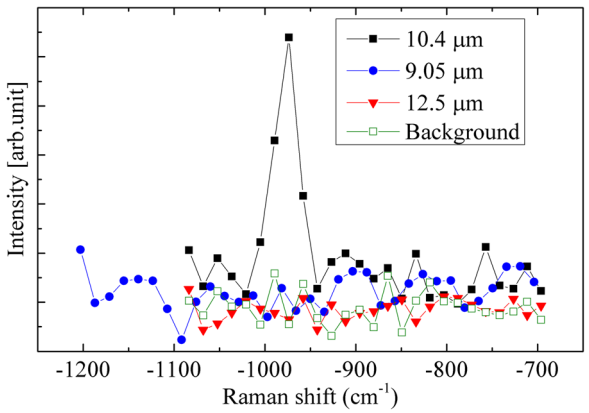

FIG. 5. Anti-Stokes Raman scattering spectra with and without MIR-FEL irradiation at 14 K.

Nd-YAG laser were 2 μs (FWHM) and 4 ns (FWHM), respectively, and the timing between MIR-FEL and Nd-YAG laser was synchronized. The photon number of MIR-FEL at 10.4 μm overlapping with Nd-YAG laser was 3.99×10^{12} photons, and these photons were used for the phonon excitation.

Figure 5 shows the anti-Stokes Raman scattering spectra with and without MIR-FEL irradiation at 14 K. When the wavelength of MIR-FEL was tuned to 10.4 μm, a peak occurred at 970 cm^{-1}. To investigate origin of the peak at 970 cm^{-1}, the anti-Stokes Raman scattering without MIR-FEL irradiation at 14 K (green open squares in Fig. 5) was measured; the peak at 970 cm^{-1} was absent. Additionally, peaks were not present for the 9.05 and 12.5 μm excitations.

To observe the thermally excited anti-Stokes Raman scattering spectrum, which is a non-mode-selective phonon excitation, we measured the anti-Stokes Raman scattering spectrum at 298 K without MIR-FEL irradiation. Two peaks were observed (Fig. 6). The peak at 970 cm^{-1} corresponded to the FLO(0) phonon mode,[16] while the one at 790 cm^{-1} corresponded to the folded transverse optical phonon mode at $x = 1/3$, which is indexed as FTO (1/3).[16] The FTO (1/3) mode is Raman active but is not infrared active. Therefore, it is impossible to excite the FTO (1/3) mode by photo-excitation method.

Table II summarizes the excitation condition and the peaks observed. A peak corresponding to the photon energy

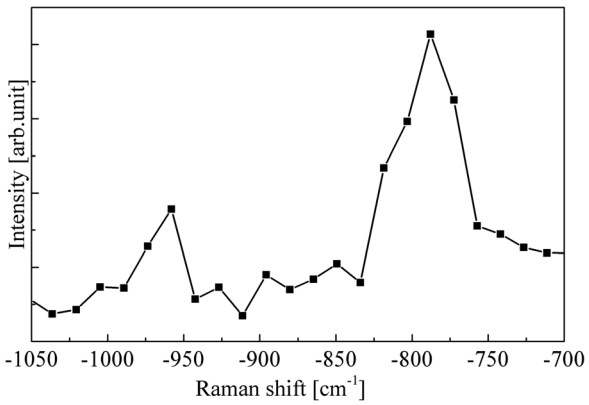

FIG. 6. Anti-Stokes Raman scattering spectra without MIR-FEL irradiation at 298 K.

TABLE II. Results for each experimental condition.

Experiment No.	Wavelength of MIR-FEL (μm)	Temperature (K)	Wave number and wavelength of peaks: cm^{-1} (μm)
1	10.4 (FLO(0) phonon mode)	14	970 (10.4)
2	9.05	14	Not observed
3	12.5 (FTO(0) phonon mode)	14	Not observed
4	Without MIR-FEL irradiation	14	Not observed
5	Without MIR-FEL irradiation	298	970, 790 (10.4, 12.7)

of the MIR-FEL was observed in anti-Stokes Raman scattering spectrum (experiment 1), but it did not originate from the SFG induced by MIR-FEL and Nd-YAG laser (experiment 2). The peak at 970 cm^{-1} occurred only when the photon energy of MIR-FEL matched the FLO(0) phonon mode (119 meV, 10.4 μm) (experiments 1 and 3). Because MIR-FEL irradiation was essential to observe the peak at 970 cm^{-1}, the peak was not induced by the effect of Nd-YAG laser irradiation (comparison of experiments 1 and 4). Moreover, phonons excited by a thermal effect resulted in two peaks (experiment 5).

In summary, the peak at 970 cm^{-1} in experiment 1 is not induced by a thermal effect through laser heating but is a photo-excitation effect. Because this peak is attributed to the selective excitation of the FLO(0) phonon mode by MIR-FEL irradiation, herein mode-selective phonon excitation by a mid-infrared laser on 6H-SiC is demonstrated by anti-Stokes Raman scattering spectroscopy.

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